Photoinduced optical anisotropy in the chalcogenide glass As_2S_3

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New photoinduced phenomena have been observed during exposure of the chalcogenide glass As_2S_3 to linearly polarized light with $h\nu < E_g$: a transmission anisotropy with nonmonotonic kinetics, an optical activity with *S*-shaped kinetics, and an ellipticity and a depolarization of the transmitted light. These phenomena are attributed to the interaction of light with the weak bonds which are characteristic of chalcogenide glasses.

In Refs. 1 and 2 we found some features in the photoinduced anisotropy of films of glassy chalcogenide semiconductors which were induced by light with a photon energy greater than the band gap ($h\nu > E_g$). It seemed important to determine whether a photoanisotropy could be induced by light with $h\nu < E_g$ in order to identify the mechanism for this photoinduced anisotropy, which is quite different from the mechanism for the photoinduced changes in scalar optical properties.[1,2] Because of the small optical absorption coefficient, a corresponding study was carried out on thick samples. This study yielded several unexpected results, which we are reporting here.

We studied samples of the monolithic glass As_2S_3, prepared by cooling a melt, with two parallel polished faces, separated by a distance which was varied over the interval 1.0–50.0 mm. We used the beam from a He–Ne laser with a photon energy $h\nu = 1.96$ eV, which satisfies the condition $h\nu < E_g$ (for As_2S_3, $E_g = 2.3$ eV; Ref. 3). The beam was focused onto the entrance face of the sample by a lens with a long focal length, into a spot 80–200 μm in diameter. The absorption coefficient for this light was ~ 0.7 cm^{-1}. We used the experimental apparatus described in Ref. 4. The properties of the transmitted light were measured at discrete times by inserting a filter in front of the sample to reduce the intensity of the incident light by a factor of ten (we will call this attenuated beam the "probe" light beam).

Curve 1 in Fig. 1 shows the relative transmission of linearly polarized light as a function of the exposure time, $I_{\parallel}(t)/I_{\parallel}(0)$. This curve shows that during prolonged exposure the transmission falls off by more than an order of magnitude. Shown by curve 2 in the same figure is the kinetics of the photoinduced anisotropy of the transmission, characterized by the ratio $2(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$ where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the probe light beam transmitted through the sample in the cases in which the probe beam is incident on the sample with electric vector respectively parallel to and perpendicular to the electric vector of the unattenuated light beam (which induces the effect). We see that the photoinduced anisotropy of the transmission is characterized by a nonmonotonic kinetics: The anisotropy initially increases, goes through a maximum, and then decreases, in fact changing sign. Note also the large values of the transmission anisotropy, which reach 20–30% at the maximum; these

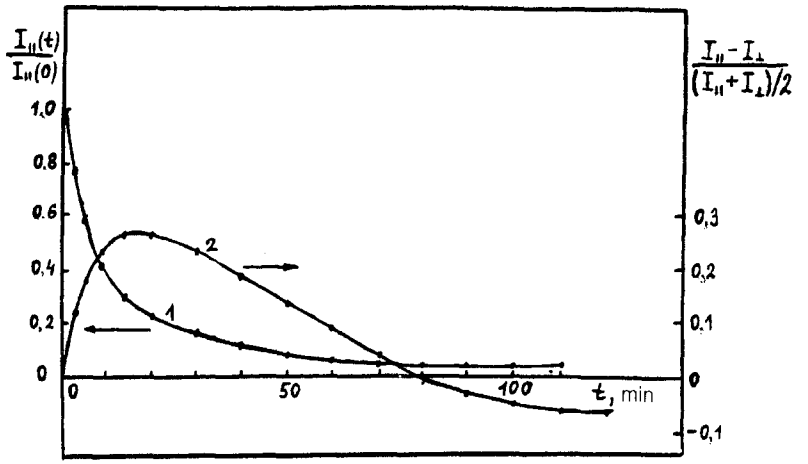

FIG. 1. Kinetics of (1) the relative transmission and (2) the anisotropy of the transmission of a probe light beam in an As_2S_3 sample 25 mm thick. The changes were induced by light with a power density of 5 W/cm^2.

values are well above those which have been observed previously in film samples of glassy chalcogenide semiconductors.[1,2]

To explain this nonmonotonic, sign-varying behavior of the transmission anisotropy—which in the case at hand could not result from interference effects, as in thin-film samples[4]—one might suggest that the polarization plane of the linearly polarized light rotates as the light passes through the bulk sample. An analysis of the polarization state carried out with the help of a $\lambda/4$ plate and a polarizer film confirmed this suggestion, revealing that the polarization plane rotated through angles γ which reached large values (curve 1 in Fig. 2). It is easy to see that for the glass As_2S_3 there is an initial rotation of the polarization plane (a natural optical activity). There is also a photoinduced change in the optical activity, whose kinetics is described by an *S*-shaped curve: The change is initially slow; it then accelerates and later slows down, as saturation sets in. The sign of the optical activity changes in the process. The existence of natural and photoinduced optical activities in the glass As_2S_3 has been noted previously by Hajto and Ewen.[5]

In the course of this study it was found that the transmitted beam undergoes not only a polarization-plane rotation but also a photoinduced change in ellipticity, characterized by the ratio of the squares of the semiaxes of the polarization ellipse, b^2/a^2. This change is shown in Fig. 2, by curve 2, which is not monotonic. The ellipticity reaches a maximum at the time corresponding to the most rapid change in the optical activity. (In the experiments we measured the analyzer rotation angle φ required to quench the transmitted light when the axis of the $\lambda/4$ plate was oriented parallel to the major axis of the polarization ellipse;[6] the analyzer rotation angle is related to the ellipticity by $\tan\varphi = b^2/a^2$.) The polarization state of the transmitted light at various times is shown schematically in the inset in Fig. 2.

The transmitted light could not be quenched entirely. The only possible reason

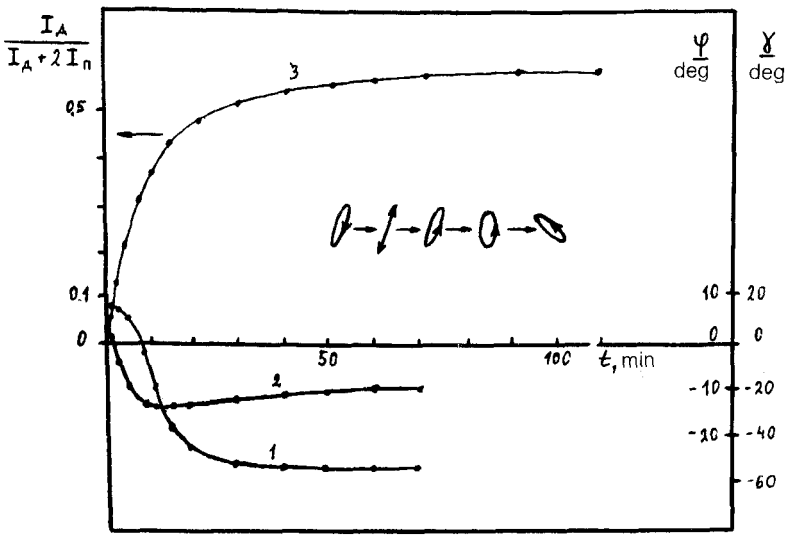

FIG. 2. Changes in (1) the optical activity γ, (2) the ellipticity φ, and (3) the depolarization under the same conditions as for Fig. 1.

would be a partial depolarization of the light. We carried out a direct determination of the depolarized component of the transmitted light by a procedure which has been used elsewhere (Ref. 6, for example). Curve 3 in Fig. 2 shows the results of these experiments on the kinetics of the depolarization, defined here as $I_d/(I_d + 2I_p)$, where I_d and I_p are the intensities of the depolarized and polarized components. We see that the transmitted light is completely polarized before the exposure to light and that the rapid increase in the depolarization occurs early in the process.

We note in conclusion that all the results shown in Figs. 1 and 2 are typical of the As_2S_3 samples which we studied and were obtained for a fixed position of the incident light beam on the surface of the sample. When we changed this position, we observed a scatter in the values and sign of the initial optical activity, in the magnitude of the ellipticity of the transmitted light, and in the nature of the kinetics of the photoinduced changes.

In summary, we have observed several new photoinduced optical phenomena in the glass As_2S_3 during excitation by light with $h\nu < E_g$.

The mechanism for these phenomena cannot involve a rupture of covalent interatomic bonds, which is responsible for the photoinduced change in the scalar optical properties of glassy chalcogenide semiconductors at $h\nu > E_g$ (Ref. 7). These phenomena should probably be attributed to an interaction of low-energy photons with weak bonds (of the Van der Waals type), which are necessarily present in glassy chalcogenide semiconductors, which are inorganic polymers. The absorption of light with $h\nu < E_g$ is a consequence of specifically these weak bonds, and it is possible that these weak bonds generate some of the intrinsic defects in a glass, characterized by localized states which lie deep in the band gap.

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